

pentaerythritol diacrylate monostearate and other polymerization curable unsaturated resins and crosslinking polymerizable unsaturated monomers or unsaturated oligomers. These polymerizable unsaturated monomers may be used alone or in a combination of two or more types.

The filler used in the present invention is either a powdered or hollow filler preferably having a mean particle size of 0.5 to 200  $\mu\text{m}$ . Examples of said powdered filler include calcium carbonate, silica, glass, alumina, clay, aluminum hydroxide, barium sulfate, calcium sulfate and quartzite, while examples of said hollow filler include organic hollow fillers (such as polyvinylidene chloride, polyvinyl chloride, polymethylmethacrylate, polymethylacrylate, polyacrylonitrile or copolymers of two or more of their types) and inorganic hollow fillers (such as glass, silica and ceramic). The particle size may be that which does not cause a problem in spraying with a sprayer during formation of the intermediate layer (B), lamination during formation of the fiber-reinforced plastic layer (C) or impregnation and degassing work. In addition, two or more types of these fillers may be used in combination. The filler is preferably a mixture of calcium carbonate powder and hollow filler. The mean particle size of the powdered filler is preferably 0.5 to 20  $\mu\text{m}$ , and more preferably 2 to 8  $\mu\text{m}$ . The mean particle size of the hollow filler is preferably 5 to 200  $\mu\text{m}$ . In addition, the amount of hollow filler added is preferably 1 to 10 parts by weight, and more preferably 1 to 5 parts by weight, with respect to 100 parts by weight of the curable resin composition.

Examples of commercially available fillers used in the present invention include the calcium carbonate NS series (manufactured by Nitto Funka Co., Ltd.), aluminum hydroxide Higilite H series (manufactured by Showa Denko K.K.), alumina (manufactured by SUMITOMO CHEMICAL CO., LTD.) and calcium sulfate Franklin Fiber (manufactured by United States Gypsum Company). Examples of commercially available hollow fillers include Scotchlite Glass Bubble (manufactured by Sumitomo-3M Co., Ltd.), Dualite (manufactured by Pierce & Stevens Co.), Glass Microballoon (manufactured by Emerspon & Cuming Co.), Q-CEL Microcel (manufactured by Asahi Glass Co., Ltd.), Expancel Microcel (manufactured by Japan Phylite Co., Ltd.) and MFL series (manufactured by Matsumoto Oil Co., Ltd.). The use of the intermediate layer composition that contains the above hollow filler is particularly preferable because antifoaming properties are improved when spraying the intermediate layer (B) onto the

back side of the surface layer (A) composed of a polymer material, and the specific gravity of said composition can be lowered.

The thixotropic agent used in the present invention may be of a form that imparts thixotropy to heat-curable resins. Specific examples include silica powders, asbestos, smectite, calcium sulfate whisker, and the like. Two or more types of the above agents may be used in combination as necessary.

Examples of commercially available thixotropic agents include REOLOSIL QS series (manufactured by Tokuyama Co., Ltd.), Aerosil series (manufactured by Nippon Aerosil Co., Ltd.), Benathix series (manufactured by Wilber-Ellis Co.), Cabosil series (manufactured by Cabot Co.), HDK series (manufactured by Wacker CO.) and Franklin Fiber (manufactured by USG Co.).

The fiber-reinforced plastic layer (C) of the present invention is provided on the previously cured intermediate layer (B) by either the hand lay up molding method, spray up molding method, or RTM (resin transfer molding) method in the same manner as fiber-reinforced plastic layers of the prior art so as to obtain the desired design strength and modulus of elasticity. Impregnation and degassing work are repeated for a polymerizable unsaturated resin composition blended with curing accelerator and curing agent into chopped strand mat and/or roving cloth having a fiber length of about 2 inches in the case of the hand lay up molding method, or into chopped strand having a fiber length of about 1 inch in the case of the spray up molding method, followed by curing at normal temperature or by heating. In addition, the RTM method involves first charging form glass mat or roving cloth and so forth into a mold followed by injection molding of a polymerizable unsaturated resin composition blended with curing accelerator and curing agent.

The polymerizable unsaturated resin composition used in the fiber-reinforced plastic layer (C) of the present invention is preferably unsaturated polyester, epoxy(meth)acrylate, urethane(meth)acrylate or a mixture thereof. Polymerizable unsaturated resins are dissolved in polymerizable unsaturated monomers, and are liquid resin compositions that can be cured at normal temperature by addition of curing accelerator and curing agent. In addition, the thixotropic agents described to follow may be added to prevent running and maintain workability, and the fillers described to follow may also be added within a range that does not impair workability and strength properties in consideration of cost, in the

same manner as ordinary hand lay up molding and spray up molding methods. Moreover, pigment may also be added as necessary.

The polymerizable unsaturated resin used in said fiber-reinforced plastic layer (C) is obtained from the raw materials of the polymerization curable unsaturated resin used in the above intermediate layer (B).

The types and amounts added of curing agents, curing accelerators and retardants may be suitably selected and used in the resin compositions used for the surface layer (A), the intermediate layer (B), and the fiber-reinforced plastic layer (C) of the present invention to adjust their curing rate.

Examples of the above curing agents include azo compounds such as azoisobutyronitrile, and organic oxides such as known diacylperoxide, peroxyester, hydroperoxide, dialkylperoxide, ketone peroxide, peroxyketal, alkylperester and percarbonate compounds, specific examples of which include methylethyl ketone peroxide and benzoylperoxide. Two or more types of these may also be used in combination. The amount added is preferably 0.5 to 5 parts by weight with respect to 100 parts by weight of the curable resin composition.

Examples of curing accelerators include metallic soaps such as cobalt naphthenate, cobalt octenoate, vanadyl octenoate, copper naphthenate and barium naphthenate, and metallic chelating compounds such as vanadyl acetylacetate, cobalt acetylacetate, and iron acetylacetate. In addition, examples of amines include N,N-dimethylamino-p-benzaldehyde, N,N-dimethylaniline, N,N-diethylaniline, N,N-dimethyl-p-toluidine, N,N-bis(2-hydroxyethyl)-p-toluidine, 4-N,N-dimethylaminobenzaldehyde, 4-N,N-bis(2-hydroxyethyl)aminobenzaldehyde, 4-methylhydroxyethylaminobenzaldehyde, N,N-bis(2-hydroxypropyl)-p-toluidine, N-ethyl-m-toluidine, triethanolamine, m-toluidine, diethylenetriamine, pyridine, phenylmorpholine, piperidine and diethanolaniline.

The amount of curing accelerator added is preferably 0.001 to 5 parts by weight with respect to 100 parts by weight of the curable resin composition. Amine-based accelerators are preferable in the present invention. Furthermore, the curing accelerator may be added to the resin in advance, or may be added at the time of use.

Examples of curing retardants include trihydrobenzene, trihydroquinone, 1,4-naphthoquinone, parabenzoquinone, hydroquinone, benzoquinone,